



## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

<b>(51) International Patent Classification <sup>5</sup> :</b>  <b>A23L 1/22, B01J 13/02</b>	<b>A1</b>	<b>(11) International Publication Number:</b> <b>WO 92/05708</b>  <b>(43) International Publication Date:</b> 16 April 1992 (16.04.92)
<b>(21) International Application Number:</b> PCT/US91/07278 <b>(22) International Filing Date:</b> 4 October 1991 (04.10.91)  <b>(30) Priority data:</b> 593,678                      5 October 1990 (05.10.90)                      US  <b>(60) Parent Application or Grant</b> <b>(63) Related by Continuation</b> US    593,678 (CIP) Filed on    5 October 1990 (05.10.90)  <b>(71) Applicant (for all designated States except US):</b> GRIFFITH LABORATORIES WORLDWIDE, INC. [US/US]; 1 Griffith Center, Alsip, IL 60658-3495 (US).		<b>(72) Inventors; and</b> <b>(75) Inventors/Applicants (for US only) :</b> JANDA, Joseph [US/ US]; 15000 South Avers Avenue, Midlothian, IL 60445 (US). BERNACCHI, Donald [US/US]; 2536 North Montclair, Chicago, IL 60635 (US). FRIEDERS, Su- zanne [US/US]; 8747 South Melvina, Oaklawn, IL 60453 (US).  <b>(74) Agent:</b> SUFRIN, Barry, W.; Laff, Whitesel, Conte & Sar- et, 401 North Michigan, Suite 2000, Chicago, IL 60611 (US).  <b>(81) Designated States:</b> AT (European patent), BE (European patent), CA, CH (European patent), DE (European pa- tent), DK (European patent), ES (European patent), FR (European patent), GB (European patent), GR (Euro- pean patent), IT (European patent), LU (European pa- tent), NL (European patent), SE (European patent), US.  <b>Published</b> <i>With international search report.</i> <i>Before the expiration of the time limit for amending the</i> <i>claims and to be republished in the event of the receipt of</i> <i>amendments.</i>
<b>(54) Title:</b> IMPROVED MICROENCAPSULATION PROCESS AND PRODUCTS  <b>(57) Abstract</b>  A microencapsulation process in which a solid or liquid core material is dispersed in a protein slurry, is heated to create a protein melt and then denatured to bring about encapsulation of the core material and the product of that process.		

**FOR THE PURPOSES OF INFORMATION ONLY**

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	ES	Spain	MG	Madagascar
AU	Australia	FI	Finland	ML	Mali
BB	Barbados	FR	France	MN	Mongolia
BE	Belgium	GA	Gabon	MR	Mauritania
BF	Burkina Faso	GB	United Kingdom	MW	Malawi
BG	Bulgaria	GN	Guinea	NL	Netherlands
BJ	Benin	GR	Greece	NO	Norway
BR	Brazil	HU	Hungary	PL	Poland
CA	Canada	IT	Italy	RO	Romania
CF	Central African Republic	JP	Japan	SD	Sudan
CG	Congo	KP	Democratic People's Republic of Korea	SE	Sweden
CH	Switzerland	KR	Republic of Korea	SN	Senegal
CI	Côte d'Ivoire	LI	Liechtenstein	SU <sup>+</sup>	Soviet Union
CM	Cameroon	LK	Sri Lanka	TD	Chad
CS	Czechoslovakia	LU	Luxembourg	TG	Togo
DE*	Germany	MC	Monaco	US	United States of America
DK	Denmark				

<sup>+</sup> Any designation of "SU" has effect in the Russian Federation. It is not yet known whether any such designation has effect in other States of the former Soviet Union.

IMPROVED MICROENCAPSULATION PROCESS AND PRODUCTSBACKGROUND OF THE INVENTION

This invention relates generally to microencapsulation and, more particularly, to microencapsulation of solids and liquids in a water-insoluble protein coating.

5           Microencapsulation is the art of encapsulating or enclosing a core comprising a solid or liquid in a miniature package called a microcapsule. The encapsulating material or coating of the microcapsule may be of various thicknesses and may be more than one layer thick.

10           Microcapsules may range from sub-micron in diameter to several millimeters in diameter. Although they are often thought of as being smooth and spherical, their shape and surface texture may be quite irregular as determined by both the encapsulating process and the shape and nature of the core material.

15           In the food industry, for example, microencapsulation is used to stabilize the core material, to control the timing and rate of the release of the core material and to separate reactive or incompatible components of a multicomponent formulation. Thus, microencapsulation makes it possible to protect sensitive  
20           food components, to ensure against nutritional loss and to mask or preserve flavors and aromas. Encapsulation also increases stability of vitamin supplements, for example, which are normally sensitive to UV radiation, light, oxygen, metals, humidity and temperature. Microencapsulation is also utilized in the  
25           pharmaceutical industry to protect the lining of the mouth and esophagus from harsh, orally administered drugs which are released in the stomach by the action of stomach acids and

- 2 -

enzymes on the microcapsule coating.

Spray drying is one of the most widely used methods of microencapsulation. This process, which involves dispersion and atomization, has a number of drawbacks. One disadvantage of the spray drying microencapsulation technique is that when heat is used for drying, low-boiling point aromatics are lost during the drying process. Another disadvantage is that the core may adhere to the surface of the capsule, presenting a potential for increased oxidation and changes in the flavor balance of the finished food product. Yet another drawback is that the coatings produced are often water-soluble and temperature sensitive.

Extrusion is an encapsulation method in which a core material is dispersed in an amorphous mass of coating material and ultimately formed into microcapsule. One such method, described in U.S. Patent No. 4,230,687 which is assigned to the assignee of the present invention, involves a microencapsulation technique in which the core material is mixed with the coating material under conditions of rigorous and intimate mechanical working in the presence of a limited quantity of water and sufficient heat to ensure the formation of a viscous semi-solid homogeneous paste constituting a plastic melt. The melt, which is a homogeneous matrix of the encased core material is formed into a desired shape and dried. The coating agent is a water-soluble or water-dispensable material such as a carbohydrate like dextrin, gum acacia and gum karaya, or a protein like gelatin (water soluble at about 160°F) or sodium caseinate.

SUBSTITUTE SHEET

- 3 -

**BRIEF DESCRIPTION OF THE DRAWINGS**

The features of this invention which are believed to be novel are set forth with particularity in the appended claims. The invention, together with its objects and the advantages thereof, may be best understood by reference to the following description taken in conjunction with the accompanying drawings, in which like reference numerals identify like elements in the several figures and in which:

FIGURE 1 is a drawing depicting iron core particles approximately 10-20 microns in diameter, under approximately 1000X magnification; and

FIGURE 2 is a drawing depicting microcapsules of the iron particles of FIG. 1 encased in a protein coating in accordance with the present invention, under approximately 500X magnification; and

FIGURE 3 is a graph illustrating the varying coating solubility achieved by varying the pH to achieve denaturization.

**SUMMARY OF THE INVENTION**

It is an object of the present invention to provide a method of microencapsulating core material comprising solids and liquids in a water-insoluble protein coating.

It is yet another object of the present invention to provide a method for producing microencapsulated products of a wide range of particle size distributions.

- 4 -

Yet another object of the present invention is to provide a method for producing microcapsules of a predetermined degree of solubility in water.

The present invention therefore comprises a method of preparing microencapsulated particles by:

- a) dispersing a core material in a soluble protein slurry;
- b) heating the slurry to create a protein melt;
- c) denaturing the protein melt to render it insoluble in water, thereby causing the encapsulation of the core material; and
- d) comminuting the encapsulated core material to provide microcapsules in which the core material is encased in an insoluble protein coating.

In one preferred embodiment, the encapsulated core material of step c) is dried before comminuting.

a. The Core Material

Core materials useful in the practice of the present invention include solids, liquids impregnated in a solid carriers such as sugar, gelatin, or maltodextrin, and liquids standing alone. In the food industry, useful core materials include acidulants, natural colors, flavoring agents and spices, leavening agents, sodium chloride, sweeteners, vitamins, minerals and vitamin precursors (e.g. beta-carotene), flavors, volatile oils and oleoresins. Examples of volatile oils are oil of acacia, oil of cloves, peppermint oil, spearmint oil, lemon oil, garlic oil, and combinations thereof. Examples of oleoresins are

- 5 -

ginger, black pepper, and paprika. Typical flavoring agents which may be encapsulated include natural and artificial flavors such as banana, cherry, strawberry, chicken, beef, sweet, savory, and fruit. Encapsulation greatly enhances the stability of these materials, particularly through high temperature/short time processing. Spices, when encapsulated, display enhanced shelf life and enhanced retention of potency, as well as inhibition of reaction with other ingredients.

Acidulants, for example, are used as flavor modifiers, preservation aids and processing aids. Unencapsulated, these materials can react with food ingredients to decrease shelf life, degrade color and flavor, and cause separation of ingredients. Encapsulation precludes or limits oxidation and provides controlled release, thereby minimizing or overcoming many of these problems. Additionally, encapsulation reduces hygroscopicity, reduces dusting and improves flowability. Acidulants that may be encapsulated in accordance with the present invention include all organic and inorganic acids including, in particular, adipic acid, ascorbic acid, citric acid, fumaric acid, lactic acid, malic acid, and acid phosphates.

Vitamins and minerals which are typically added to fortify a variety of foods, including breakfast foods, dairy products, infant formulas and pet foods, may be encapsulated to reduce off-flavors, to permit timed-release and to reduce susceptibility to extremes in temperature and moisture and reactions with other ingredients. Among the vitamins and minerals which may be

SUBSTITUTE SHEET

- 6 -

encapsulated in accordance with the process of the present invention are: ascorbic acid, niacin, vitamin B6, riboflavin, thiamine, vitamin B12, vitamin A, vitamin E, folic acid, vitamin D, phrenic acid, biotin, copper, iron, potassium, zinc, phosphorous, and beta carotene.

The particle size of the core material is dictated by the application. For example, when iron is encapsulated for use as a dietary supplement, bioavailability concerns dictate that the iron core be less than 44 microns in diameter. Iron core particles 10 and 12 approximately 10-20 microns in cross-section are depicted in FIGURE 1 under about 1000X magnification.

#### b. The Coating

The coatings may be formed from any animal or vegetable protein which is water-soluble, water-dispersible, or capable of being solubilized. Examples of proteins useful in the practice of the intervention are listed below:

Protein class	Examples
Dairy proteins and their salts	casein, caseinate, milk albumin, whey
Cereal proteins	corn protein, soy, wheat gluten, rice gluten, rye gluten, barley gluten, oat gluten, sorghum gluten
Meat proteins	acto myosin, collagen, gelatin
Egg protein	egg albumin
Soybean proteins	soy concentrate, soy isolate, soy flour



- 7 -

The following proteins are preferred as coatings in the practice of the present invention: caseinate, soy concentrate, soy isolate, soy flour, wheat gluten, egg albumin, milk albumin, gelatin, zein (corn protein), and combinations of any two or more of these.

c. The Encapsulation Process

The core material to be encapsulated must first be dispersed in an aqueous slurry of the protein coating including water at a level in the range of about 10 to 200% by weight, based on the weight of the core material, with a level of about 50% by weight water preferred. Calcium stearate may optionally be added at a level of about 10 to 30% by weight to improve the pliability of the resulting product. The core material may range from about 5 to 70% by weight, preferably from about 25 to 40% by weight and most preferably at about 30% by weight. Any method of obtaining a uniform dispersion can be used.

In a preferred practice of the present invention, an extruder is used in which the protein and core material are introduced into the extruder feed hopper and dispersed by the vigorous working and sheering action of the rotating extruder screws.

Once a uniform dispersion is obtained, the protein slurry is heated to a temperature sufficient to form a melt. Again, in a preferred embodiment of the invention, the heating step is carried out in an extruder in which the melt is formed under the requisite heating conditions of the extruder.

- 8 -

When the protein is sodium caseinate and the core material is iron at a level of about 30% by weight, a melt may be formed by heating in the temperature range of about 85-250°F, preferably in the range of about 100-200°F and most preferably in the range of about 135-155°F.

The protein melt is then denatured, which renders it water-insoluble and brings about the encapsulation of the core material.

Denaturization may be accomplished by or with the addition of acid to adjust the pH to the isoelectric point of the protein, with proteolytic enzymes, heat, or alkaline agents. Denaturization either with pH adjustment to the isoelectric point or with proteolytic enzymes is presently preferred in the practice of the invention.

#### (I) pH Adjustment

When the protein coating is sodium caseinate, and denaturization is carried out by pH adjustment, the pH should be adjusted down to about 6.0, preferably down to about 5.0 and most preferably to about pH 4.6.

In an alternative embodiment of the invention, denaturization is carried out by adjustment of the pH downwardly to a point short of the isoelectric point of the protein, to tailor the degree of insolubility of the protein to the desired application. FIGURE 3 is a graph illustrating the tailoring of the solubility of the coating by varying the pH during denaturization.

- 9 -

(II) Enzymes

In yet another alternate approach, a proteolytic enzyme which renders protein insoluble, may be used. Any proteolytic enzyme that will denature and coagulate the coating protein can be used. Examples of proteolytic enzymes useful in the practice of the invention for this purpose include:

ficin  
bromelin  
papain  
chymopapain  
pepsin  
rennin  
trypsin  
chymotrypsin  
elastase  
bacterial protease  
fungal protease  
collagenase

Ficin, bromelin, papain and chymopapain are preferred proteolytic enzymes in the practice of the invention.

The coagulation step will preferably be carried out for a period long enough to essentially eliminate all soluble protein. Digestion of the protein should be avoided. This point can be determined by a conventional protein solubility determination test. Coagulation will be terminated by subjecting the mixture to sufficient heating to deactivate the enzyme. This may be done, for example, in a dryer such as a fluid bed dryer or a ring dryer, or in an oven. Denaturization using proteolytic enzymes will be especially preferred where high concentrations of fat are present since acidity will not develop.

- 10 -

The enzyme will typically be used in the form of an aqueous solution containing from about 0.1 to 1.0% by weight of the enzyme and the temperature of the mixture of protein slurry and enzyme will be kept under close control to avoid heat deactivation of the enzyme. Alternatively, partial heat deactivation may be sought in certain circumstances, as where there is a combination of different enzymes which deactivate at different temperatures, thereby limiting the degree of denaturization and tailoring the degree of insolubility of the final encapsulated product.

The proteolytic enzymes show enhanced coagulation activity in the presence of a  $\text{Ca}^{+2}$  a  $\text{Mg}^{+2}$  salt, with calcium salts being preferred. Useful calcium salts include:

- calcium chloride ( $\text{CaCl}_2$ )
- calcium lactate
- calcium glyconate
- calcium citrate
- calcium sulfate
- calcium phosphate
- calcium tartrate

Among these "activation" compounds,  $\text{CaCl}_2$  is preferred. The level of  $\text{Ca}^{+2}$  based on protein should be at least about 0.5% by weight and preferably about 1.5% by weight. Excess  $\text{CaCl}_2$  is not generally detrimental except insofar as it might have adverse taste effects. The levels of activation compounds other than  $\text{CaCl}_2$  will have to be determined on a case-by-case basis.

SUBSTITUTE SHEET

- 11 -

d. Comminution

Next the encapsulated material is comminuted into a granular form, with the core material remaining encapsulated in the insoluble protein, as illustrated in FIGURE 2, in which the coating is depicted by the numeral 14 and iron particles corresponding to those shown in FIGURE 1 are depicted by the numeral 16. In a preferred embodiment, the encapsulated material is first dried. Typically drying will be done by heating the material to a temperature below about 350°F. When sodium caseinate is coated on an iron core, the drying temperature should be below about 325°F and preferably below about 300°F.

Particle size reduction is accomplished by wet milling, for example in a Mikawa mill, by hammer milling of dry material and by centrifugal extrusion.

EXAMPLES

As explained above, the method of the present invention is effective in microencapsulating many different types of core materials in various coatings, over a broad range of concentration ratios of coatings to core material. In the illustrative examples which follow, the ratio of coating to core material, in parts by weight, embraces the range of from about 5 to about 70. Since the objectives of the present invention can be accomplished with conventional equipment, including commercially available mixers and extruders, no detailed

- 12 -

description of the apparatus is provided. Rather, the following examples are described with reference to various types of suitable, commercially available equipment.

Example 1

5 In this example, particulate iron of from about 10 to 20 microns in diameter, as illustrated in FIGURE 1, was dispersed in a soluble protein slurry of sodium caseinate, by blending in a ribbon blender. The mixture also contained calcium stearate to improve pliability of the end product and various colorants.  
10 The slurry comprised the following levels of these components, in percentages by weight:

	Iron	30.0%
	Calcium Stearate	10 0
	Sodium Caseinate	49.1
15	Titanium Dioxide	10.0
	Yellow #6 (17%)	.72
	Yellow #5 (25%)	<u>4.0</u>
		100%

Once the core material was dispersed in the slurry using a  
20 Baker-Perkins extruder (a twin screw extruder), the slurry was heated to about 90°F to create a protein melt. The protein melt was then denatured (and hence precipitated) by adding sufficient hydrochloric acid to adjust the pH down to about pH 4.6. The denatured protein was then wet ground in a Mikawa mill to reduce  
25 average particle size to about 180 microns, which in turn reduced the drying time.

The precipitate was then dried by heating in a pan drier to 300°F for about 20 minutes and the dried precipitate was further comminuted in a hammer mill into a granular form having an

- 13 -

average particle size of about 90 microns. The resulting product, illustrated in Figure 2, comprised iron particle microcapsules with about 85% encapsulation.

#### Example 2

5 In this example, mixtures of soluble proteins and soluble carbohydrates are examined as the encapsulating matrix. Thus, if sodium caseinate is combined with hydrolyzed cereal solids in a ratio of about one to one by weight, and the process of Example 1 were carried out using this protein/carbohydrate combination  
10 with a flavoring agent such as oil of cloves at the core, a controlled flavor release would result when the encapsulated material is placed in a aqueous media.

#### Example 3

Another technique for controlling the solubility of the  
15 coating of the microcapsule is examined in this example. Thus, if the method of Example 1 were followed but the pH during the denaturing process were adjusted to about pH 5.6, the coating would be partially soluble in water. Such a product would have about a 35 percent by weight solubility in water, as seen in  
20 FIGURE 3.

#### Example 4

Yet another technique for controlling the solubility of the coating is explored in this example, namely varying the temperature and/or the use during denaturization with a  
25 proteolytic enzyme. Thus, the procedure of Example 1 could be generally followed but denaturization carried out using ficin at

- 14 -

pH of 5.5, to achieve a tailored solubility. Alternatively, if an activator such as cystine hydrochloride, or a chemical inhibitor such as sorbic acid could be used to tailor the solubility.

5

Example 5

In this Example, a series of alternative solid and liquid core materials as well as a variety of coatings are set out in formulas which, if combined in accordance with the practice of Example 1 would produce useful microencapsulated products in accordance with the present invention. All figures are in percentages by weight.

I.

15	Soy Protein Isolate	64
	Calcium Stearate	10
	Iron	25
	TiO <sub>2</sub>	1.0

II.

20	Soy Protein Concentrate	64
	Calcium Stearate	10
	Iron	25
	TiO <sub>2</sub>	1.0

III.

25	Egg Whites (Dried)	64
	Calcium Stearate	10
	Iron	25
	TiO <sub>2</sub>	1.0

IV.

30	Sodium Caseinate	63
	Calcium Stearate	10
	TiO <sub>2</sub>	20
	Beta Carotene (30%)	2.0
	Caramel Color	5.0



- 15 -

V.

5	Vitamin Premix	25	
	Calcium Stearate		10
	Sodium Caseinate		50.6
	TiO <sub>2</sub>	14	
	Yellow #6	0.4	

VI.

10	Magnesium Chloride (Anhydrous)	12.5	
	Zinc Stearate		10.0
	Encapsulating Protein		77.5

VII.

15	Copper Gluconate		5.0
	Calcium Stearate		10.0
	Encapsulating Protein		85.0

VIII.

20	Oil of Orange		20.0
	Calcium Stearate		10.0
	Encapsulating Protein		70.0

EXAMPLE 6

This example generally paralleled Example 1 except that a series of proteolytic enzymes were used to coagulate the sodium caseinate in lieu of the hydrochloric acids and the slurry comprised, in percentages by weight:

25	Iron	28.0%
	Sodium Caseinate	58.42
	Titanium Dioxide	10.0
	Yellow #6 (17%)	0.8
	Yellow #5 (25%)	0.4
30	Cystine hydrochloride	0.04
	Ficin	0.04
	Calcium Chloride	2.3

- 16 -

The enzymes and the relevant parameters are set out in the table below:

5	Encyme	Optimum Activation Temperature (°F)	Optimum pH	Time	Conc. (% by weight)	Milk Clotting Units
	Ficin	122°	5.5	30 sec.	0.07	-
	Papain	145°	6.0	60 sec.	0.07	-
10	Bromelin	122°	6.5	60 sec.	0.07	-
	Chymosin	100°	5.5	30 min.	0.8	88
	M. Pusillus Protease	100°	5-5.5	30 min.	0.4	228
15	M. Miehl Protease	100°	5-5.5	30 min.	0.8	115
	E. Parasitica Protease	98	5-5.5	30 min.	0.4	180

In all cases a good encapsulated product was obtained.

While the present invention is described above in connection with the preferred or illustrative embodiments, those embodiments are not intended to be exhaustive or limiting of the invention. Rather, the invention is intended to cover any alternatives, modifications or equivalents that may be included within its sphere and scope, as defined by the appended claims.

- 17 -

What We Claim Is:

1. A method of microencapsulating a core material comprising:

- a) dispersing the core material in a protein slurry;
- 5       b) heating the slurry to create a protein melt;
- c) denaturing the protein melt, thereby causing encapsulation of the core material; and
- d) comminuting the encapsulated core material to provide microcapsules.

10       2. The method of claim 1 wherein in the core material is chosen from the group consisting of solids, liquids, and liquids impregnated in solid carriers.

15       3. The method of claim 1 wherein the core material is chosen from the group consisting of acidulants, natural colors, flavoring agents, spices, leavening agents, sweeteners, vitamins, minerals, vitamin precursors, flavors, volatile oils and oleoresins.

20       4. The method of claim 1 wherein in the core material is chosen from the group consisting of oil of acacia, oil of cloves, peppermint oil, spearmint oil, lemon oil, garlic oil, and combinations thereof.

5       5. The method of claim 1 wherein in the core material is chosen from the group consisting of ginger, black pepper, and paprika.

- 18 -

6. The method of claim 1 wherein in the core material is chosen from the group consisting natural and artificial flavors of banana, cherry, strawberry, chicken, beef, sweet, savory, and fruit.

5           7. The method of claim 1 wherein in the core material is chosen from the group consisting of adipic acid, ascorbic acid, citric acid, fumaric acid, lactic acid, malic acid, and acid phosphate.

10           8. The method of claim 1 wherein in the core material is chosen from the group consisting of ascorbic acid, niacin, vitamin B6, riboflavin, thiamine, vitamin B12, vitamin A, vitamin E, folic acid, vitamin D, phrenic acid, biotin, copper, iron, potassium, zinc, phosphorous, beta carotin, and combinations of two or more thereof.

15           9. The method of claim 1 wherein in the core material is iron particles.

          10. The method of claim 9 in which the iron particles are less than 44 microns in diameter.

20           11. The method of claim 1 in which the protein of the protein slurry is chosen from the group consisting of caseinate, soy concentrate, soy isolate, soy flour, wheat gluten, egg albumin, milk albumin, gelatin, zein, rice gluten, wheat gluten, barley gluten, oat gluten, rye gluten, and sorghum gluten, and combinations of two or more thereof.

25           12. The method of claim 1 in which the protein of the protein slurry is caseinate.

- 19 -

13. The method of claim 1 in which the protein slurry includes water at a level in the range of about 10 to 200% by weight, based on the weight of the core material.

14. The method of claim 1 in which the protein slurry  
5 includes water at a level in the range of about 50% by weight, based on the weight of the core material.

15. The method of claim 1 in which calcium stearate is added at a level of about 10 to 30% by weight, based on the weight of the core material.

10 16. The method of claim 1 in which the core material is present in a range of about 5 to 70% by weight.

17. The method of claim 1 in which the core material is present in a range of about 25 to 40% by weight.

15 18. The method of claim 1 in which the core material is present at about 30% by weight.

19. The method of claim 1 in which the core material is dispersed in the protein slurry using an extruder.

20 20. The method of claim 1 in which the protein slurry containing the core material is heated in an extruder to create a protein melt.

21. The method of claim 1 in which the protein is sodium caseinate and the core material is iron.

22. The method of claim 21 in which the iron is present at  
a level of about 30% by weight and the melt is formed by heating  
25 in the temperature range of about 85-250°F.

- 20 -

23. The method of claim 22 in which the melt is formed by heating in the temperature range of about 100-200°F.

24. The method of claim 22 in which the melt is formed by heating in the temperature range of about 135-155°F.

5 25. The method of claim 1 in which the denaturization is carried out by treating the protein melt with an agent chosen from the group consisting of proteolytic enzymes, heat, alkaline agents, to adjust the pH to the isoelectric point of the protein.

10 26. The method of claim 1 in which the denaturization is carried out by treating the protein melt with acid to adjust the pH to the isoelectric point of the protein.

27. The method of claim 1 in which the protein of the protein slurry is sodium caseinate and denaturization is carried out by adjusting the pH of the protein melt to about pH 6.0.

15 28. The method of claim 1 in which the protein of the protein slurry is sodium caseinate and denaturization is carried out by adjusting the pH of the protein melt to about pH 5.0.

20 29. The method of claim 1 in which the protein of the protein slurry is sodium caseinate and denaturization is carried out by adjusting the pH of the protein melt to about pH 4.6.

30. The method of claim 1 in which the denaturization of the protein melt is carried out by adjusting the pH downwardly to a point short of the isoelectric point of the protein, thereby tailoring the degree of the insolubility of the protein.

- 21 -

31. The method of claim 25 in which the proteolytic enzyme is chosen from the group consisting of ficin, bromelain, papain, chymopapain, pepsin, rennin, trypsin, chymotrypsin, elastase, bacterial protease, fungal protease, and collagenase.

5        32. The method of claim 31 in which the proteolytic enzyme is used in the form of an aqueous solution containing from about 1.0 to about 1.0% by weight of the enzyme.

10       33. The method of claim 31 in which a combination of different enzymes which deactivate at different temperatures is used, and the combination is partially heat deactivated to limit the degree of denaturization, thereby to tailor the degree of insolubility of the final encapsulated product.

      34. The method of claim 1 in which the protein melt is dried before comminuting.

15       35. The method of claim 34 in which the drying is accomplished by heating to a temperature below about 350°F.

      36. An microencapsulated product prepared by performing the steps of:

- 20       a) dispersing a core material in a protein slurry;  
      b) heating the slurry to create a protein melt;  
      c) denaturizing the protein melt, thereby causing encapsulation of the core material; and  
      d) comminuting the encapsulated core material.

25       37. The method of claim 31 in which the proteolytic enzyme is chosen from the group consisting of ficin, bromelain, papain and chymopapain.

      38. The method of claim 31 in which the proteolytic enzyme is ficin.

39. The method of claim 1 in which denaturization is carried out by treating the protein melt with one or more proteolytic enzymes in the presence of a salt of  $\text{Ca}^{+2}$  or  $\text{Mg}^{+2}$ .

40. The method of claim 39 in which a  $\text{Ca}^{+2}$  salt is used.

5 41. The method of claim 39 in which the salt is present at a level sufficient to supply at least about 0.5% by weight of the  $\text{Ca}^{+2}$  or  $\text{Mg}^{+2}$  ion, based on the weight of the protein.

10 42. The method of claim 39 in which the salt is present at a level sufficient to supply at least about 1.5% by weight of the  $\text{Ca}^{+2}$  or  $\text{Mg}^{+2}$  ion, based on the weight of the protein.



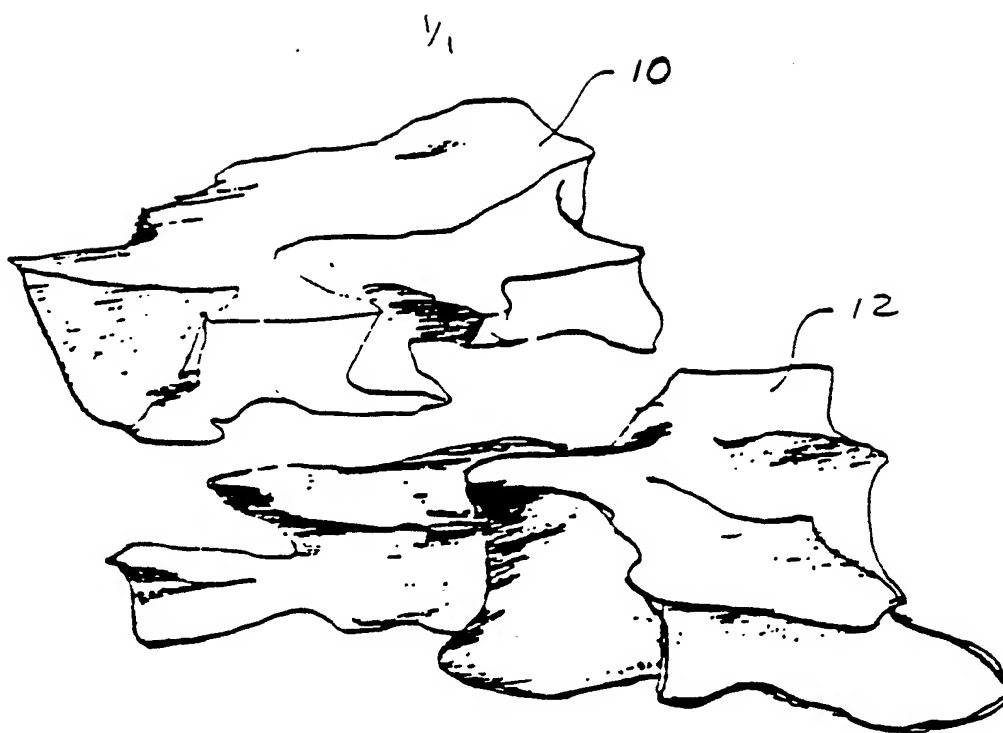


FIG. 1

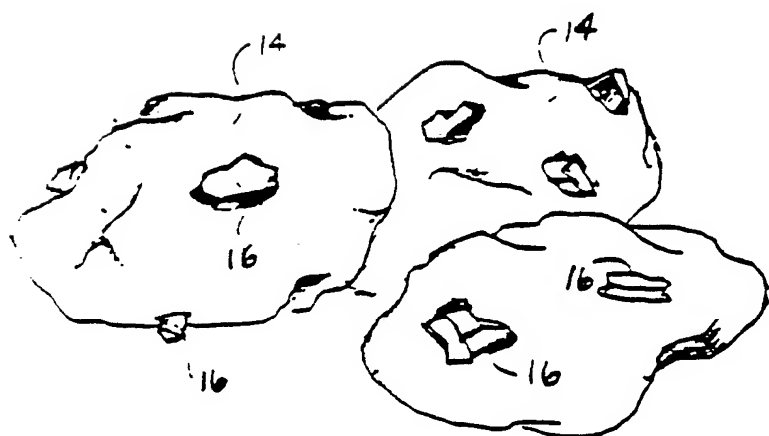
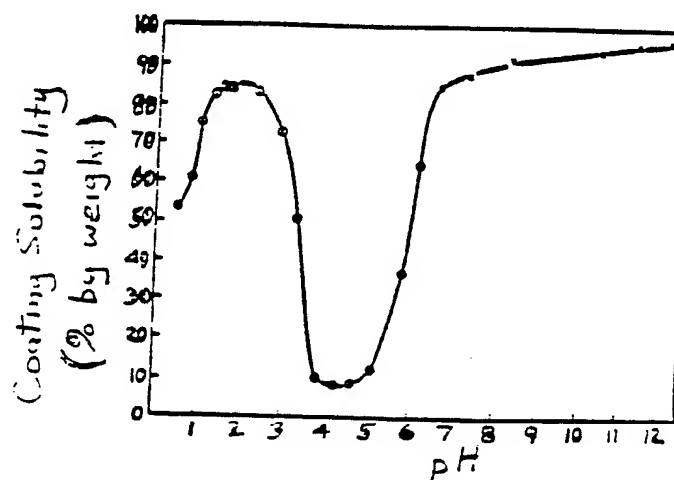


FIG. 2

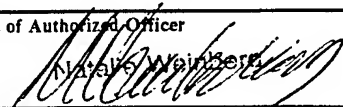
FIG. 3



# INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 91/07278

<b>I. CLASSIFICATION OF SUBJECT MATTER</b> (if several classification symbols apply, indicate all) <sup>6</sup>		
According to International Patent Classification (IPC) or to both National Classification and IPC Int.C1.5                      A 23 L    1/22                      B 01 J    13/02		
<b>II. FIELDS SEARCHED</b>		
Minimum Documentation Searched <sup>7</sup>		
Classification System	Classification Symbols	
Int.C1.5	A 23 L                      B 01 J	
Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched <sup>8</sup>		
<b>III. DOCUMENTS CONSIDERED TO BE RELEVANT<sup>9</sup></b>		
Category <sup>o</sup>	Citation of Document, <sup>11</sup> with indication, where appropriate, of the relevant passages <sup>12</sup>	Relevant to Claim No. <sup>13</sup>
X	US,A,4232047 (L. SAIR et al.) 4 November 1980, see column 3, lines 47-64; column 4, lines 5-18; column 4, lines 50-55; column 5, lines 2-38; column 6, lines 22-32; column 15, lines 8-39; column 1, lines 15-48  ---	1-6,8, 11,13, 14,16- 20,22- 24,34, 35,36
X	US,A,4428927 (W.R. EBERT et al.) 31 January 1984, see column 2, lines 14-27; column 2, lines 42-43; column 2, lines 54-60  ---	1-4,6, 11,13, 24,25, 34,35, 36
A	GB,A, 569345 (GENERAL FOODS CORP.) 18 May 1945, see page 2, lines 102-124; page 3, lines 2-19; page 3, lines 43-52; page 6, lines 120-128; page 7, lines 39-43; page 9, lines 74-93; page 10, lines 19-38  -----	1,2,3, 11,25, 26,32
<div style="display: flex; justify-content: space-between;"> <div style="width: 45%;"> <p><sup>o</sup> Special categories of cited documents : <sup>10</sup></p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> </div> <div style="width: 45%;"> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to underscore the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"&amp;" document member of the same patent family</p> </div> </div>		
<b>IV. CERTIFICATION</b>		
Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report	
14-01-1992	26.02.92	
International Searching Authority	Signature of Authorized Officer	
EUROPEAN PATENT OFFICE	 Name: [illegible]	

**ANNEX TO THE INTERNATIONAL SEARCH REPORT  
ON INTERNATIONAL PATENT APPLICATION NO.**

US 9107278  
SA 53047

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report. The members are as contained in the European Patent Office EDP file on 04/02/92. The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US-A- 4232047	04-11-80	None	
<hr/>			
US-A- 4428927	31-01-84	US-A- 4532126	30-07-85
		AU-B- 559817	19-03-87
		AU-A- 2238483	20-06-85
		CA-A- 1209039	05-08-86
		DE-A- 3347386	11-07-85
		FR-A,B 2557429	05-07-85
		GB-A,B 2151201	17-07-85
		JP-A- 60139617	24-07-85
<hr/>			
GB-A- 569345		None	
<hr/>			